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(58) Field of search
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Selected US specifications from IPC sub-class
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(54) Electroless silver plating compositions

(57) An electroless silver plating composition comprises an aqueous solution of a soluble silver salt with an organic complexing agent for silver ions, preferably containing carboxylate or nitrogen ligands. The presence of the complexing agent enables the silver to be deposited in metallic form when the composition is applied to a metal surface and the water allowed to evaporate. Suitable complexing agents are ethylenediamine tetraacetic acid, acetic acid, saccharine or succinimide. Silver is however also prevented from precipitating from the solution during storage. The composition may also include a reducing agent such as sorbitol as well as a surfactant, a suspending agent, abrasives and polishing agents, and finds application in replating of silver plated articles such as fishknife blades or a silver plated salt dish with the copper substrate revealed by applying the composition to their surface accompanied with rubbing.

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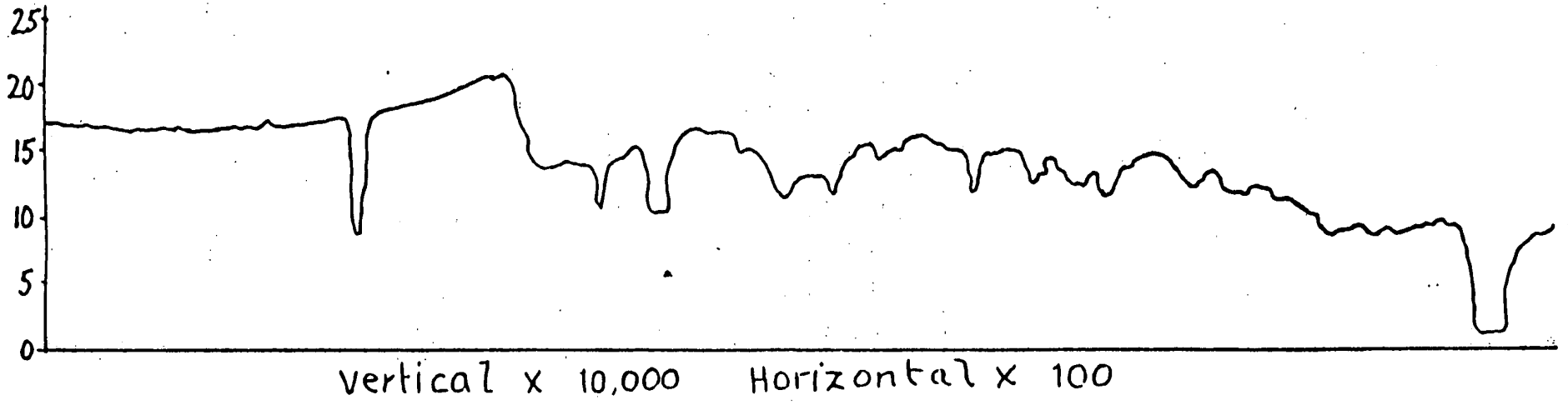

Fig.1

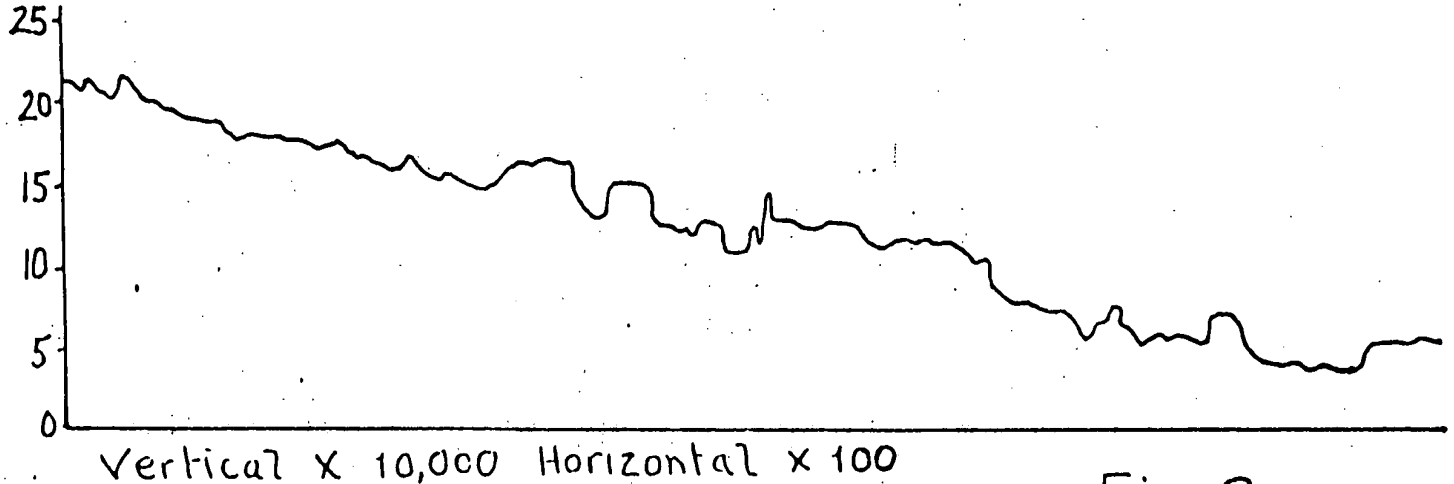

Fig.2

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ELECTROLESS SILVER PLATING COMPOSITIONS

This invention relates to a silver-containing composition and in particular to a composition which can be used for the polishing and simultaneous replating of silver-plated articles as well as for the electroless silver plating of base metals.

Silver surfaces are subject to tarnishing, which is a black deposit of silver sulphide caused by the reaction of the silver with hydrogen sulphide in the atmosphere. Conventional polishes for removing the tarnish generally involve abrasives or chemical reagents which inevitably remove a small amount of the silver. In the case of silver plated articles this can eventually lead to the exposure of the base metal substrates.

Until recently plated articles on which the silver plating had become unacceptably thin had to be replated either by electrolysis or by electroless plating using silver salt compositions which had to be up in situ and could not be stored. For example British Patent 1603675 of Perovetz et al discloses and claims a process for simultaneously polishing and restoring silver-plated articles using a paste comprising a silver salt such as silver nitrate and a reducing agent which precipitates silver. The composition has to be in dry powder form and mixed to a paste just prior to use, as otherwise the reducing agent would cause the silver to precipitate out of solution during storage instead of during polishing. Canadian patent no. 930902 of Young and Mueller discloses an aqueous electroless plating solution containing a silver salt and sodium cyanide. The complex thus formed keeps the silver in solution while enabling it to plate out as metallic silver when the solution is applied to a substrate and the water evaporated. The solution is however toxic, at least by ingestion, in view of the presence of cyanide ions.

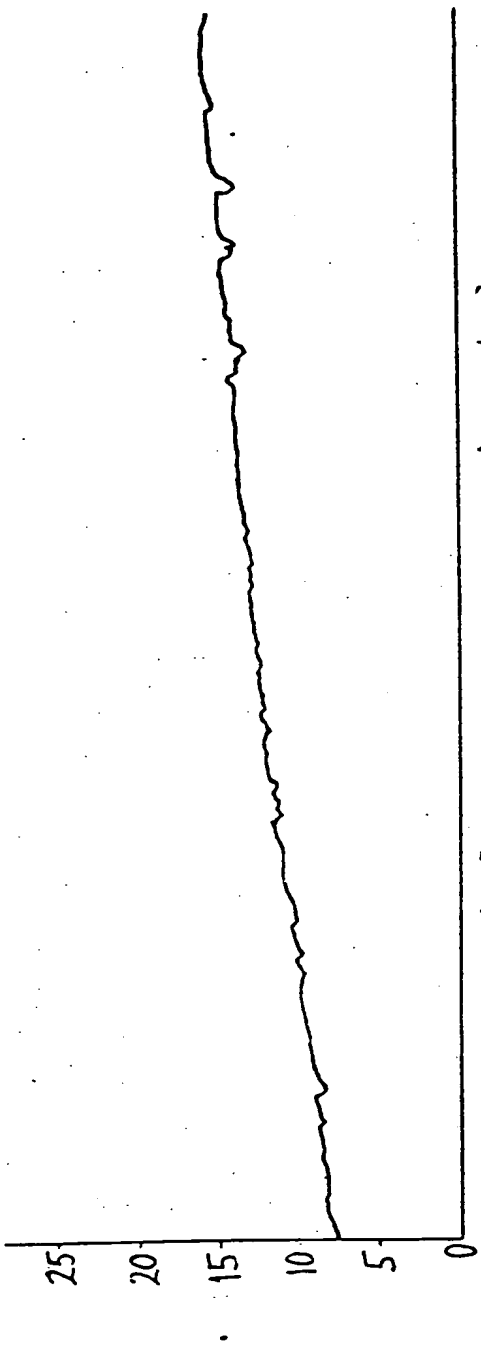

Fig.3

The composition may also include a reducing agent if desired, since the presence of the complexing agent will prevent silver from being precipitated out of solution. A wide variety of such reducing agents can be used, the main criteria being non-toxicity and removal from the plated surface. Preferred reducing agents are reducing sugars, more preferably sorbitol. This may be included in the solution in an amount from 0.5 to 4 wt.%, and preferably not more than 2%. The composition may also include conventional mild abrasives and polishing agents such as diatomaceous earth, bentonite or kieselguhr. These components may suitably comprise 5 to 25 wt.% of the total composition, or preferably 10 to 15 wt.%.

Other components which may be included are surfactants and suspending agents. These include hydroxyethyl cellulose, stearic acid/triethanolamine adduct and cationic surfactants.

The preferred embodiments of the invention will now be illustrated by the following examples.

Example 1.

An aqueous plating solution is made up having the following composition:

Silver Nitrate	- 1.0 wt.%
Acetic Acid	- 0.01 wt.% as Glacial)
Sorbitol	- 1.5 wt.%
Diatomaceous Earth	- 10 - 15 wt.%
Stearic Acid/ triethanolamine suspending agent	- 1 - 1.5 wt.%
Water	- balance.

The diatomaceous earth is added, in the form of a suspension in the stearic acid/triethanolamine adduct, to a hot aqueous solution of the other ingredients. This composition has been found to give excellent results, replacing silver in the plated layer at least as quickly as it is removed by polishing. Furthermore, the composition has an excellent

The present invention consists in an electroless silver plating composition comprising an aqueous solution of soluble silver salt and an organic complexing agent for silver ions.

It is possible by means of the invention to provide an electroless silver plating composition in the form of an aqueous solution, which does not contain toxic ingredients but which is stable for long term storage and in which the silver ions remain in solution and do not precipitate before the solution is applied.

The composition of the invention can be applied to substrate using a cloth, cotton wool or the like and allowed to dry. The silver plates on to the substrate and other components of the composition are then rubbed off as in the case of a conventional polish.

The preferred silver salt is silver nitrate but other silver salts may be used provided they have sufficient water solubility. Other silver salts which could be used include silver halides and silver acetate. The silver salt is preferably present in an amount from 0.2 to 5 wt.% based on the total solution, the preferred maximum being about 2.5%. A concentration of 1 to 2% has been found particularly suitable.

The complexing agent is preferably one with carboxylate or nitrogen-containing ligands, for example acetic acid or ethylenediamine tetraacetic acid (EDTA). The use of toxic silver complexing agents such as cyanides and phosphines is thus avoided. The complexing agent is preferably present in an amount from 5×10^{-4} to 0.5 mole/litre, more preferably 0.005 to 0.2 mole/litre. In the case of acetic acid the preferred content is 0.002 to 0.05 wt.%, suitably 0.01 wt.% whereas in the case of EDTA the preferred range is 0.5 to 3 wt.%.

Other complexing agents which may be used include organic imides such as succinimide and saccharine.

in the surface caused by the combined chemical/mechanical affect of the plating composition and the rubbing.

SURFACE ROUGHNESS MEASUREMENT.

A first blade, part of one side of which was treated with the composition of Example 2 had its surface finish tested by causing a fine stylus to pass across the boundary of the original electroplated surface and onto the replated surface. The trace thus obtained is shown in Figure 1 of the accompanying drawings. In this figure the vertical magnification of 10,000 times is 100 times greater than the horizontal magnification so that the surface roughness relative to the area being tested is exaggerated by a factor of 100. The left hand part of the trace represents the original electroplated area (which was in virtually new condition and mirror polished) whereas the rest of the trace represents the area replated by manual application of the composition of the invention. Despite the increased roughness shown by such measurement the appearance of the replated area was good although less bright than that of the electroplated silver. The contrast would be much less marked on an article which had been used for a considerable time and was in need of replating and would also be far less noticeable on a non-flat surface.

Figures 2 and 3 of the drawings represent respectively the worst and best surface roughness traces obtained with a second blade which was subjected to two 30 second applications of the composition of Example 2. It can be seen that the surface of the best area is nearly as smooth as that of the original electroplating shown in Figure 1, whereas even the worst area (near the stamp mark and edge of the blade) has relatively little surface roughness. The difference between these two areas may be attributable to variations in the amount of rubbing each area received, but in any case there was no visible difference between the two areas, the appearance of which was good.

shelf life, comprising as it does a stable complex of silver ions in solution.

Example 2.

An electroless plating solution was made up having the following composition:

Kieselguhr	- 11.0 wt.%
Hydroxylmethyl Cellulose	- 0.06 wt.%
Cationic Surfactant	- 0.2 wt.%
Silver Nitrate	- 2.0 wt.%
EDTA	- 2.2 wt.%
Bentonite	- 0.25 wt.%
Water	- 83.4 wt.%.

The composition of Example 2 was applied to fishknife blades of electroplated nickel silver (EPNS) which is a copper-zinc-nickel alloy electroplated with silver. The tests were carried out by the Cutlery and Allied Trades Research Association of Sheffield, England. Knife blades were used because being flat, their surfaces could be examined under a metallurgical microscope, at up to 900 times magnification and their surface roughness could be measured at magnification up to ten thousand times.

For part of each side of the blades, silver was removed by polishing on a rotating calico wheel.

The best method of application was found to comprise 30 seconds of heavy rubbing with a soft cloth kept well wetted with the solution, the composition being wiped off immediately. Extension of the rubbing time to 60 seconds or repetition of the 30 seconds treatment, tended to remove some of the silver deposited by the first treatment, thereby imparting a yellowish colour to the plated area.

The treated surfaces of the blades had a good appearance, although on microscopic examination they were found to have small unplated islands (typically 0.018 x 0.0038 mm) which appeared to coincide with microdepressions

the composition by fairly heavy rubbing for at least 30 seconds with a cloth or cotton wool dipped in the plating composition to ensure that the surface being treated is kept wet. When the surface is seen to be completely covered with silver the rubbing should be discontinued and any excess composition thoroughly wiped off. Over application or too much rubbing was liable to remove deposited silver.

It was also found that prior to applying the composition of the invention it was not necessary to remove any tarnish from the original silver plating becuase the composition of the invention also acted as an excellent detarnishing agent.

APPLICATION TO BRASS

A 25 cm cast brass candleholder was silver plated by application of the composition of Example 2. Close examination with the naked eye and under a four times magnifying lens, under conditions of illumination selected to reveal any variations in colour, showed complete coverage with silver.

APPLICATION TO COPPER

Part of an old silver plated salt dish, with silver plate worn off the base of the interior and the decoration to reveal the copper substrate, was treated by applying the composition of Example 2 by rubbing with cotton wool. The treated area inside the dish was approximately 40 cm^2 and the time of application to this part was five minutes. It was found however that this application time was somewhat too long because silver began to come off again. It was however found that after wiping off and repeating the whole of the over-treated area could be replated.

The decorative rim of the dish was very heavily embossed with deep nooks and crannies. It appears that in order to plate the deepest areas without losing silver from the more prominent parts, a material other than cotton wool, for example a soft brush, would be preferable.

The final result within the salt dish bowl was good to the naked eye and matched up well with the residual electroplated silver. Even some deep corrosion spots caused be deliquescing table salt left in the bowl could be plated to some extent.

Tests were also carried out on the handle of a copper plated spoon that had not previously been silver plated. Coverage with silver complete to the naked eye was achieved in 60 seconds.

The conclusion of the above tests was that the composition of the invention is particularly suitable for replating areas of decorative plated silverware from which the original silver has become worn. The best method appeared to be to apply

12. A composition according to claim 11, wherein said reducing agent is sorbitol.

13. A composition according to claim 12, wherein sorbitol is present in an amount from 0.5 to 4 wt.%.

14. A composition according to any preceding claim, further comprising an abrasive.

15. A composition according to claim 14, wherein the abrasive is selected from diatomeceous earth, bentonite and kieselguhr.

16. A composition according to any preceding claim, further comprising a suspending agent.

17. A composition according to claim 16, wherein said suspending agent comprises a stearic acid/triethanolamine adduct.

18. A composition according to claim 16 wherein said suspending agent comprises hydroxymethyl cellulose.

19. A method of forming a silver plated layer on a metallic substrate which comprises the steps of applying to a surface of said substrate a composition according to any preceding claim and rubbing the composition onto said substrate to deposit a layer of silver.

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CLAIMS

1. An electroless silver plating composition comprising an aqueous solution of soluble silver salt and an organic complexing agent for silver ions.

2. A composition according to claim 1, wherein the silver salt is silver nitrate.

3. A composition according to claim 1 or claim 2, wherein the silver salt is present in an amount from 0.2 to 5 wt.% based on the total solution.

4. A composition according to any preceding claim wherein the complexing agent is a carboxylate group-containing compound.

5. A composition according to claim 4, wherein the complexing agent is ethylenediamine tetraacetic acid. (EDTA).

6. A composition according to claim 5, wherein the EDTA is present in an amount of 0.5 to 3 wt.%.

7. A composition according to claim 4, wherein the complexing agent is acetic acid.

8. A composition according to claim 7, wherein the acetic acid is present in an amount from 0.002 to 0.005 wt.%.

9. A composition according to any one of claims 1 to 3 wherein the complexing agent is an imide compound.

10. A composition according to claim 9, wherein the complexing agent is saccharine or succinimide.

11. A composition according to any preceding claim further comprising a reducing agent.